HIGH ENERGY OXIDIZERS

CONTRACT Nonr-4019(00)

Project NR 093-035

Richmond Research Center
Richmond, California

AD 424714

STAUFFER CHEMICAL COMPANY
Richmond Research Center
Richmond, California

"HIGH ENERGY OXIDIZERS"

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Summary

One compound, $ClF_2^+AsF_6^-$, was selected from the chlorine-trifluoride based complexes and investigations were concentrated on this single compound. Low temperature NMR, X-ray investigations, conductometric titration and molecular weight determinations were carried out and the ionic structure seems to be proven with reasonable certainty.

Abstract

This is the third Quarterly Technical Summary Report on our investigation on chlorinetrifluoride based complexes.

Some modification was made on the vacuum line to allow its use in conductometric titration and molecular weight determination. At the same time a dry-box was assembled for use with chlorinetrifluoride and similar corrosive materials.

Low temperature NMR work was repeated, but only qualitative proof was obtained for the ionic structure. The dissociation of the complex was measured in IF_5 and found to be complete within the error of the measurement. The ionic structure was proved by conductometric titration too.

The Debye-Scherrer powder diagram was obtained for both $KAsF_6$ and $ClF_2^+AsF_6^-$. ~~Investigations are not yet finished on this field.~~

Introduction

In order to prove the ionic structure of chlorinetrifluoride based complexes NMR and IR investigations were made in the previous quarter. Only qualitative observations could be made from the results because of the fast fluorine exchange between the solvent, ClF_3, and the complexes. Investigations were continued at lower temperatures but no quantitative conclusions could be made from the results. Other methods, such as classical molecular weight determinations and conductometric titration, were the most promising ones to show the dissociation of these complexes.

Discussion

Vacuum Line and Dry-Box

The vacuum line was modified to adapt it to molecular weight determination and conductometric titration. A Dry-Box was set up for handling the necessary chemicals under anhydrous conditions because of their hygroscopic nature. The transparent parts of the Dry-Box were covered by thin Teflon sheet. The metal parts were covered by a thin film of heavy Fluorocarbon-oil in order to prevent corrosion. Satisfactory results could be obtained under such conditions.

Nuclear Magnetic Resonance

The $ClF_2^+AsF_6^-$ complex was prepared again in chlorinetrifluoride as solvent for low temperature NMR investigations. A sample of pure ClF_3 also was submitted. Earlier investigations(1) claim a triplet and a doublet for pure ClF_3 at low temperature which transforms to one broad peak if the smallest impurity was present. Chlorinetrifluoride was purified repeatedly, but only one broad unresolved peak could be obtained even at -83°C., its freezing point. No fine structure could be observed with the complex in chlorinetrifluoride solution. The splitting was obtained by the authors cited above in Teflon tubes and metal vacuum line. This procedure might assure less impurities in the samples, but no proof is available that the glass is responsible for not obtaining the fine structure.

Solubility

One of the biggest problems in the investigation of ClF_3 based complexes is the lack of inert solvents other than halogenfluorides, since it reacts with almost anything. Commercial iodinepentafluoride was purified and the solubility of different compounds in it was investigated. It is miscible with ClF_3, it dissolves considerable amount of AsF_5 and even more $ClF_2^+AsF_6^-$. Potassium fluoride has limited solubility, while forming KIF_6, but NaF is almost completely insoluble. Some solubility was observed in the case of $KAsF_6$, but

(1) Hamer, A. N., Leece, J., Bentley, P. G., United Kingdom Atomic Energy Authority, Industrial Group, 1 GR-TN/CA-1048 p. 10

less than with KF. In the case of BrF_3, similar solubilities were observed, but the main problem was the purification of BrF_3. In glass a relatively fast reaction was noted and the influence of the impurities on the conductivity can not be excluded. Therefore, IF_5 was used in the following experiments.

Freezing Point Depression

The molar freezing point depression of IF_5 was determined using KF. Attempts with NaF and $KAsF_6$ failed because of their limited solubility in IF_5 as mentioned above. Iodinepentafluoride forms KIF_6 rapidly with KF, which is a known ionic compound. Therefore, it can be supposed with reasonable certainty that it is dissociated in IF_5 completely, if it is present in small concentrations. Based on this assumption a value of 7.165°C/mol was found for the molar freezing point depression constant of IF_5 in the following equation:

$$\Delta T = \frac{\Delta T_m \cdot g \cdot 1000 \cdot [1 + (n-1)\alpha]}{M \cdot G_o}$$

where ΔT_m = molar freezing point depression constant

g = weight of dissolved compound in gr

G_o = weight of solvent in gr

M = molecular weight of dissolved compound

α = dissociation coefficient

n = number of particles forming at the total dissociation of one molecule of the dissolved compound

From this equation almost total dissociation was found in a nearly 0.1 molar solution. Since the solution is conductive the dissociation must give ionic particles and not ClF_3 and AsF_5 which could not contribute to the conductivity upon the solution of the complex in IF_5.

Conductometric Titration

Since the solution of $ClF_2^+AsF_6^-$ in IF_5 is conductive, a change in the conductivity could be observed while titrating with a suitable titer. If the complex reacts with $K^+IF_6^-$ in IF_5 solution the following reaction will take place:

$$ClF_2^+ + IF_6^- \longrightarrow ClF_3 + IF_5$$

Chlorinetrifluoride and iodinepentafluoride are not conductive either separately or in mixture. Therefore, first the complex should be replaced by $K^+AsF_6^-$. This actually involves the replacement of the ClF_2^+ cation by a K^+ cation, which process would not change too much the conductivity. When all the complex will be replaced a jump is expected in the conductivity upon the addition of excess $K^+IF_6^-$ solution.

The titration showed this jump at the place calculated from the concentration within the limit of experimental errors. First a small increase in the conductivity was observed which is also in agreement with the ionic structure, since the K^+ cation should have a higher ionic mobility than the ClF_2^+ cation. Figure 1 gives the titration curve. Since the titration was carried out with a relatively high increase of volume because of the limited solubility of KIF_6 in IF_5, the results were corrected by a factor of $V_o/V_o + \Delta V$, where V_o is the starting volume and ΔV is the added volume of KIF_6 solution. In such way almost completely straight lines were obtained.

Structure Investigation by X-Ray

The X-Ray investigation of the ClF_2^+ complexes was limited to the Debye-Scherrer powder technique, since the growing of single crystals of the ClF_2^+ based complexes from ClF_3 solutions was connected with too many experimental difficulties.

The crystal structure of complex fluorides of general formula $A^IB^VF_6$ is relatively well investigated[2]. It was found that these compounds fall into five structural types and that the structure adopted depends on the size of the ion A^I and B^V.

In the case of the hexafluoroarsenates the following structure type dependence of the cation radius was found:

TABLE I

Increasing cation radius ↓

Li $[AsF_6]$ Na $[AsF_6]$	rhombohedral, Li$[SbF_6]$ type (slightly distorted NaCl structure)	coord. number 6
Ag $[AsF_6]$ O_2 $[AsF_6]$[3]	cubic facecentered, NaCl type	coord. number 6
K $[AsF_6]$ Tl $[AsF_6]$ Rb $[AsF_6]$ Cs $[AsF_6]$	rhombohedral, K$[OsF_6]$ type (distorted CsCl structure	coord. number 8

(2) A summary of all the work done is given by: R. D. W. Kemmitt, D. R. Russell, D. W. A. Sharp, J. Chem. Soc. 1963, 4408

(3) Thiokol, Report RMD 5009-Q3 (Oct. 1962-Jan. 1963)

If it could be found that the crystal structure of the $[ClF_2^+][AsF_6^-]$ is in agreement with this radius dependency of the cation, this would be an additional proof that the $[ClF_2^+][AsF_6^-]$ actually has a hexafluoroarsenate anion and therefore an ionic structure.

The powder diagram of $K[AsF_6]$ was taken and found to be in agreement with the literature[(4)].

The powder diagram of $[ClF_2^+][AsF_6^-]$ was also taken and attempts to index it were started. Table II gives the diffraction pattern of $[ClF_2^+][AsF_6^-]$.

TABLE II

Powder diagram of $[ClF_2^+][AsF_6^-]$

Cu α rad., Ni Filter - 3 hr. 45 KV 20 mA

Uncorr 2Θ		dA°	Θ	$\sin^2 \theta$
106.7-90.1 = 16.6	strong	5.34	8.30	.0209
-88.4 = 18.9	weak	4.84	9.15	.0253
-85.6 = 21.1	very strong	4.21	10.55	.0335
-83.4 = 23.3	weak	3.81	11.65	.0408
-82.8 = 23.9	medium	3.72	11.95	.0429
-78.9 = 27.8	medium	3.21	13.90	.0577
-77.1 = 29.6	weak	3.02	14.80	.0653
-74.2 = 32.5	very weak	2.75	16.25	.0783
-73.2 = 33.5	very weak	2.67	16.75	.0831
-70.7 = 36.0	weak	2.49	18.00	.0955
-69.6 = 37.1	very weak	2.42	18.55	.1012
-63.6 = 43.1	very weak	2.097	21.55	.1349
-63.0 = 43.7	weak	2.070	21.85	.1385
-61.7 = 45.0	very weak	2.013	22.50	.1464
-56.8 = 49.9	weak	1.826	24.95	.1780
-55.6 = 51.1	weak	1.786	25.55	.1860
-51.5 = 55.2	very weak	1.663	27.60	.2146
-50.2 = 56.5	very weak	1.627	28.25	.2239

(4) R. B. Roof, Octa Cryst. (1955) 8, 739

Experimental

Dry-Box and Vacuum Line

A metal Dry-Box with plexiglass windows was modified in the following way: All plexiglass parts were covered with a transparent 0.05 mm thick Teflon sheet, which was held in place by Teflon tapes. The metal parts were covered by a thin film of Halocarbon 13-21 heavy oil. No vacuum was used, only purge with carefully dried nitrogen in both the working area and the inlet chamber. This precaution combined with the use of the vacuum line was sufficient to handle the reagents under anhydrous conditions.

Nuclear Magnetic Resonance

Samples of $ClF_2^+AsF_6^-$ in chlorinetrifluoride for NMR studies were prepared in similar way described in earlier reports. The investigations were carried out at low temperature (down to -80°C.) with no quantitative proof for the ionic structure.

Solubility

The commercial BrF_3 and IF_5 had the following specific conductance respectively: $8.5 \cdot 10^{-3}$ and $1.3 \cdot 10^{-4}$ cm^{-1} ohm^{-1}. Both were distilled under vacuum in the glass vacuum line. The conductivity of BrF_3 did not change, but that of IF_5 decreased to $1.2 \cdot 10^{-5}$ cm^{-1} ohm^{-1}. Distilled IF_5 was colorless and it could be kept in glass at dry-ice temperature for a long time without essential change in its conductivity. This distilled IF_5 was used to determine the qualitative solubility of various inorganic compounds in it. Volatile materials such as ClF_3 and AsF_5 were condensed into it from the vacuum line. Solid materials such as KF, NaF, $KAsF_6$ and $ClF_2^+AsF_6^-$ were added to the IF_5 in the conductivity cell and the liquid was stirred by a magnetic stirrer for half an hour.

When chlorinetrifluoride was added no change was observed in the conductivity. With NaF, similarly only a minor change was noted. A slurry formed at less than 0.1 molar concentration. It was stirred by a magnetic stirrer for two hours but the NaF did not dissolve. With $KAsF_6$ again a slurry was obtained at the beginning, which very slowly cleared up. Potassiumfluoride took only a short time, but it was not soluble in larger quantities. Finally, $ClF_2^+AsF_6^-$ was dissolved instantaneously forming even a molar solution. This gives the following order of solubility:

$$NaF < KAsF_6 < KIF_6 < ClF_2^+AsF_6^-$$

Freezing Point Depression

A standard all glass equipment with a glass joint connection to the vacuum line was used for these measurements. A magnetic stirrer insured a uniform temperature distribution. The freezing point of IF_5 was determined with an accuracy of $\pm$ 0.005°C. The following experiments were carried out:

Potassium fluoride was powdered in the Dry-Box and 0.1137 g. of it was dissolved in 23.55 g. of IF_5. In repeated determinations a decrease of 1.213°C in the freezing point of IF_5 was observed. Since KF forms KIF_6 with IF_5 only 23.12 g. should be counted as a solvent. Finally, it is known that KIF_6 is an ionic compound and therefore it is logical to assume that it is completely dissociated to K^+ and IF_6^- in diluted IF_5 solutions. From these values the following equation can be written for the molar freezing point depression.

$$T_m = \frac{1.213 \times 58.1 \times 23.12}{0.1137 \times 1000 \times 2} = 7.165°C$$

In another experiment 0.5748 g. of $ClF_2^+AsF_6^-$ was dissolved in 24.99 g. of IF_5 and 1.250°C freezing point depression was observed. The following feeezing point depression and change in the conductivity should be expected in the case of:

		ΔT theory	Conductivity
A.	Ionic compound, completely dissociated	1.257°C	conductive
B.	Coordination complex, undissociated	0.628°C	non-conductive
C.	Decomposition to AsF_5 and ClF_3	1.257°C	non-conductive

Since a freezing point depression of 1.250°C and a conductivity in the 10^{-2} to 10^{-3} cm^{-1} ohm^{-1} order was found, there is no doubt left that the possibilities B and C must be excluded. Therefore, it can be stated that the $ClF_3 \cdot AsF_5$ complex exists in IF_5 solution in the ionic form as ClF_2^+ and AsF_6^-.

Conductometric Titration

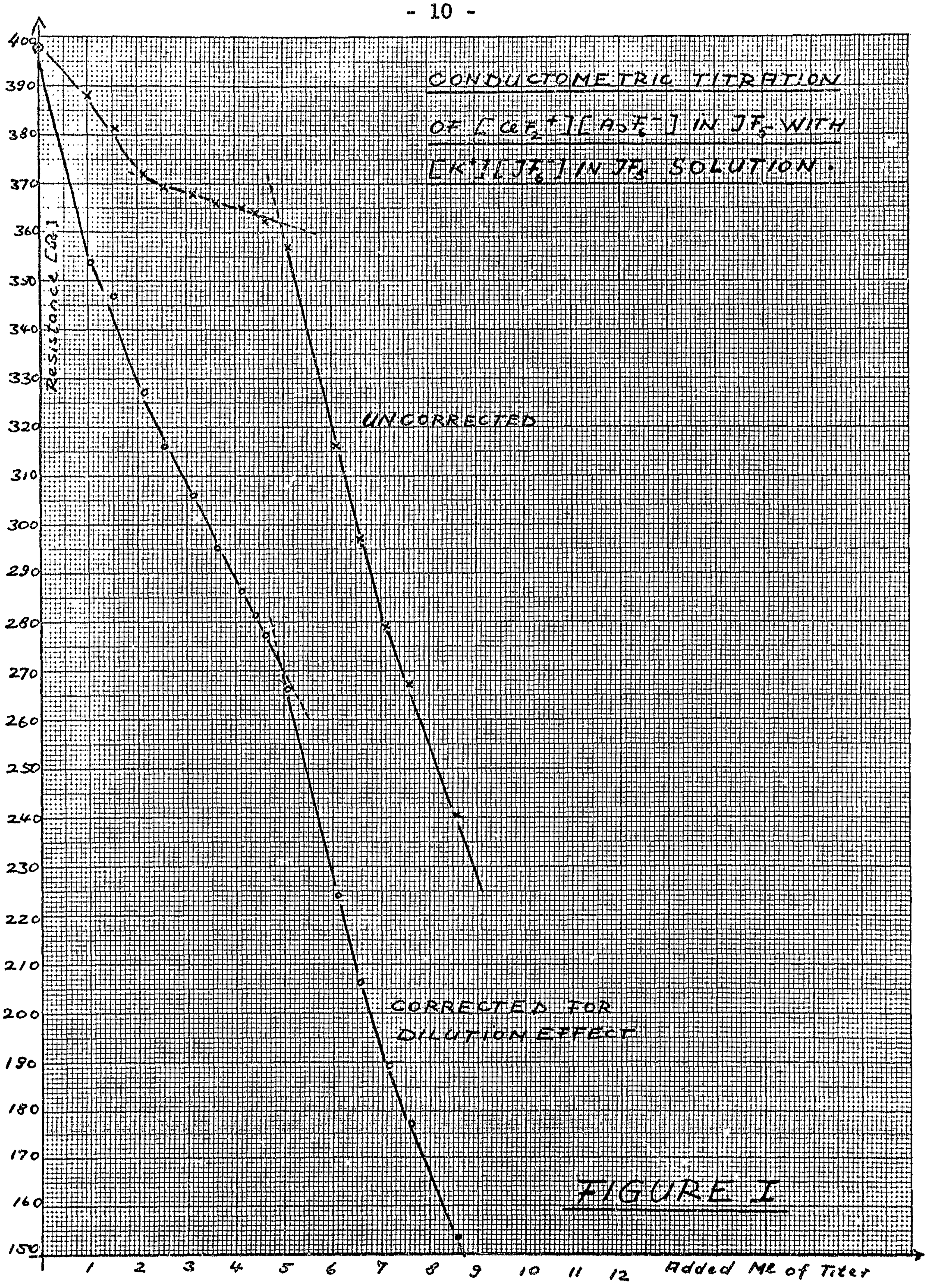
An approximately 0.1 molar KIF_6 solution in IF_5 was prepared (f = 1.15) by dissolving 0.1948 g. of KF in 93.46 g. of IF_5. The density of IF_5 at the working temperature (296°K) was calculated (from the equation d = 4.38 - 0.004T) to be 3.20 g./cm^3. This gives a concentration of 6.7 mg KIF_6/ml.

A standard conductometric cell was modified in such way that it could be connected to the vacuum line and the titration could be carried out with the exclusion of air moisture. A quantity of 0.1460 g. of $ClF_2^+AsF_6^-$ was dissolved in 48.1 g. of IF_5 (approximately 15 ml.). Under such conditions the equivalence point should be

$$\frac{58.1 \times 146.0}{262.4 \times 6.7} = 4.84 \text{ ml.}$$

The result of the conductometric titration is 4.93 ml., supposing ionic structure of the complex. The curve is shown in Figure 1 together with the corrected one which takes into consideration the dilution effect.

AEP:ls
November 26, 1963


CONDUCTOMETRIC TITRATION
OF [ClF_2^+][AsF_6^-] IN IF_5 WITH
[K^+][IF_6^-] IN IF_5 SOLUTION.
Resistance [Ω]
UNCORRECTED
CORRECTED FOR
DILUTION EFFECT
Added Ml of Titer
FIGURE I